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Doping and cluster formation in diamond

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Introducing a cluster formation model, we provide a rational fundamental viewpoint for the difficulty to achieve *n*-type doped diamond. We argue that codoping is the way forward to form appropriately doped shallow regions in diamond and other forms of carbon such as graphene. The electronegativities of the codopants are an important design criterion for the donor atom to efficiently donate its electron. We propose that the nearest neighbour codopants should be of a considerably higher electronegativity compared to the donor atom. Codoping strategies should focus on phosphorous for which there are a number of appropriate codopants. © 2011 American Institute of Physics. [doi:10.1063/1.3633223]

In the past decades, new forms of carbon (fullerenes, nanotubes, graphene) and a fresh look on the well known forms (diamond and graphite) have constituted one of the most promising classes of materials for numerous applications including nano- electronics.^{1,2} Diamond is an ideal material for many electronic applications due to its wide band gap, high carrier mobility, thermal conductivity, and electric breakdown, as well as low dielectric constant.^{3–5}

For most devices, both *n*-type (donor) and *p*-type (acceptor) doped regions are required. In the case of diamond an acceptor region can be achieved by boron (B) doping, with the acceptor level about 0.37 eV below the valence band maximum.⁶ Conversely, the material is compromised by the absence of an appropriate (shallow) donor. Both nitrogen (N) and phosphorous (P) are rather problematic.^{7–9} In particular, N (one more valence electron than C) does not contribute to the conduction band but leads to the formation of a lone electron pair on N and a dangling bond on one of its nearest neighbour C atoms. Experimentally, it has been determined that the unpaired electron is localized more on a C nearest neighbour atom than on the N donor atom.¹⁰ In practical terms the deep donor level of the N atom with an activation energy of 1.7 eV (Refs. 7 and 8) leads to almost zero excitation of electrons into the conduction band at room temperature, which in turn implies that the device cannot function in an efficient way. Comparatively, P has a shallower donor level of 0.6 eV and therefore is deemed to be a more appropriate donor.^{11,12}

From a fundamental point of view, simple considerations such as the Pauling electronegativity¹³ can explain the localization of the unpaired electron near the N atom. C (electronegativity 2.55) is less electronegative than N (electronegativity 3.04) and charge therefore is transferred from C to N. Conversely, in the case of *p*-type doping of diamond, where dopants such as boron (B) or gallium (Ga) have

smaller electronegativities than C, charge will be transferred from B (or Ga) to C. This has been determined in B doped graphene layers where there is a σ electron localization on the C atoms.¹⁴

Recent electronic structure calculations¹⁵ for silicon (Si) predicted that donor atoms such as P do not just donate an electron to the conduction band as commonly expected.¹⁶ It is rather the charge redistribution within a cluster consisting of the P atom and its four nearest neighbour Si atoms (PSi₄) and not the isolated P atom that donates the electron.¹⁵ This viewpoint is consistent with Pauling electronegativity,¹³ which dictates that P should donate an electron to the more electronegative Si atoms. Can these fundamental concepts be applied to C in order to explain the difficulties in achieving donor doping?

We apply well established electronic structure calculations¹⁷ based on density functional theory to address the effects of doping in diamond. In our calculations, we employ a $2 \times 2 \times 2$ supercell of the cubic diamond unit cell. The supercell therefore is likewise cubic with a lattice parameter of $a = 7.41$ Å and contains altogether 64 C atoms. We use a plane wave cutoff given by $RK_{\text{max}} = 8$ and a muffin-tin radius of 1.41 Å. The C 2s orbitals are treated as semicore states. Moreover, a $5 \times 5 \times 5$ mesh with 39 points in the irreducible wedge is used for the Brillouin zone integration. For the exchange correlation functional we apply the generalized gradient approximation.

We first consider doping with N as well as the effect of removing an electron from N doped diamond. The left hand side of Fig. 1 illustrates the electron density difference between a neutral NC₆₃ cell (i.e., one N dopant and 63 C atoms) and a positively charged NC₆₃⁺ cell (i.e., one N dopant and 63 C atoms minus one electron). It is evident that the N atom rather accumulates charge from its four nearest neighbour C atoms, thus forming an NC₄ cluster. The cluster formation is an important extension of the conventional donor picture, i.e., the naive expectation that one electron

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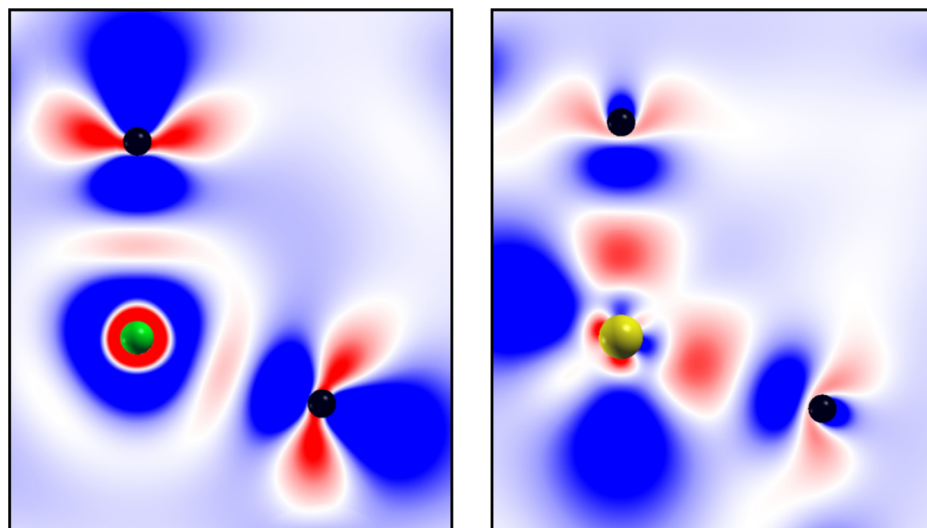


FIG. 1. (Color online) Electron density map of the (110) plane of diamond showing the difference between (left side) a neutral NC_{63} supercell and a positively charged NC_{63}^+ supercell and (right side) a neutral PC_{63} supercell and a positively charged PC_{63}^+ supercell. Small black spheres mark C atoms and larger (green/yellow) spheres mark N/P dopant atoms. Darker shade (blue colour) indicates where charge is lost. For N doped diamond, a strong loss affects the C atoms, whereas N rather accumulates charge. The opposite holds for P doped diamond.

would be donated to the crystal. It rationalizes the poor donor properties of N observed in diamond.¹⁰

In previous investigations,¹⁸ diamond also has been doped with P, leading to shallower donor levels. This observation can be explained by the fact that the Pauling electronegativity of P is 2.19 and therefore lower than that of C (2.55). Consequently, the donated electron is localized in the vicinity of the C atom. Nevertheless, the donor level of P is still rather deep, resulting in only a small number of conduction electrons. The right hand side of Fig. 1 shows the electron density difference between a neutral PC_{63} cell and a positively charged PC_{63}^+ cell. The situation is remarkably different to the N case. This is a consequence of the P atom donating electronic charge, which is confined to the nearest neighbour C atoms, and a PC_4 cluster is formed.

Electronic structure calculations therefore explain the difficulty of achieving *n*-type doped diamond. Typically, to overcome doping difficulties in semiconductors codoping strategies are employed.^{19–21} In diamond, a popular codoping strategy is the formation of donor-acceptor clusters.^{22–24} By the clusters the solubility of desirable doping atoms can be enhanced (via the Coulomb coupling between the donor and acceptor), whereas the defect level concentration can be reduced (via the donor and acceptor level repulsion).^{22–24} For example, the N-B-N cluster that has been proposed by Katayama-Yoshida *et al.*²² reduces the donor level of a single N to 1.17 eV. This change is mainly due to the delocalization of the donor electron wavefunction into the N-B-N cluster, which prevents bond breaking and restricts atomic distortion from the N substitutional site. (Note that N substitutionals in diamond exhibit bond breaking due to the pseudo Jahn-Teller interaction.²²) This, however, is not sufficient for the activation at room temperature. Notably, the Pauling electronegativity of B (2.04) is significantly lower than that of N (3.04). In fact, only fluorine (F), oxygen (O), and chlorine (Cl) reveal higher Pauling electronegativities than N. Conversely, there are numerous elements that exhibit higher electronegativities than P. The control of the dopants and

defect clustering is necessary to achieve *n*-type doped diamond.

Both for N and P doping we calculate the formation of clusters consisting of the dopant atom and the four nearest neighbour C atoms. On the basis of our data, engineering the defect processes by incorporating codopants with an appropriate electronegativity would result in doped shallow regions in diamond and other forms of carbon such as graphene. We predict that nearest neighbor codopants with a considerably higher electronegativity than the donor atom will be an important design criterion for an efficient charge donation. In that respect, N is confined by its very high Pauling electronegativity. As a consequence, we propose that future codoping strategies should focus on P, where there are more options open.

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